

conformal dielectric materials, substrates, infiltration layers, coatings, and other layering or filling materials used for producing layered stacks, electronic components, or semiconductors.

Preferably, the present compositions are used in micro-electronic applications as etch stops, hardmasks, and dielectrics. Layers or films of the instant compositions may be formed by solution techniques such as spraying, rolling, dipping, spin coating, flow coating, chemical vapor deposition (CVD), or casting, with spin coating being preferred for microelectronics.

For chemical vapor deposition (CVD), the composition is placed into an CVD apparatus, vaporized, and introduced into a deposition chamber containing the substrate to be coated. Vaporization may be accomplished by heating the composition above its vaporization point, by the use of vacuum, or by a combination of the above. Generally, vaporization is accomplished at temperatures in the range of 50° C.-300° C. under atmospheric pressure or at lower temperature (near room temperature) under vacuum.

Three types of CVD processes exist: atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD), and plasma enhanced CVD (PECVD). Each of these approaches had advantages and disadvantages. APCVD devices operate in a mass transport limited reaction mode at temperatures of approximately 400° C. In mass-transport limited deposition, temperature control of the deposition chamber is less critical than in other methods because mass transport processes are only weakly dependent on temperature. As the arrival rate of the reactants is directly proportional to their concentration in the bulk gas, maintaining a homogeneous concentration of reactants in the bulk gas adjacent to the wafers is critical. Thus, to insure films of uniform thickness across a wafer, reactors that are operated in the mass transport limited regime must be designed so that all wafer surfaces are supplied with an equal flux of reactant. The most widely used APCVD reactor designs provide a uniform supply of reactants by horizontally positioning the wafers and moving them under a gas stream.

In contrast to APCVD reactors, LPCVD reactors operate in a reaction rate-limited mode. In processes that are run under reaction rate-limited conditions, the temperature of the process is an important parameter. To maintain a uniform deposition rate throughout a reactor, the reactor temperature must be homogeneous throughout the reactor and at all wafer surfaces. Under reaction rate-limited conditions, the rate at which the deposited species arrive at the surface is not as critical as constant temperature. Thus, LPCVD reactors do not have to be designed to supply an invariant flux of reactants to all locations of a wafer surface.

Under the low pressure of an LPCVD reactor, for example, operating at medium vacuum (30-250 Pa or 0.25-2.0 torr) and higher temperature (550-600° C.), the diffusivity of the deposited species is increased by a factor of approximately 1000 over the diffusivity at atmospheric pressure. The increased diffusivity is partially offset by the fact that the distance across which the reactants must difusive increases by less than the square root of the pressure. The net effect is that there is more than an order of magnitude increase in the transport of reactants to the substrate surface and by-products away from the substrate surface.

LPCVD reactors are designed in two primary configurations: (a) horizontal tube reactors; and (b) vertical flow isothermal reactors. Horizontal tube, hot wall reactors are the most widely used LPCVD reactors in VLSI processing. They are employed for depositing poly-Si, silicon nitride,

and undoped and doped SiO₂ films. They find such broad applicability primarily because of their superior economy, throughput, uniformity, and ability to accommodate large diameter, e.g., 150 mm, wafers.

The vertical flow isothermal LPCVD reactor further extends the distributed gas feed technique so that each wafer receives an identical supply of fresh reactants. Wafers are again stacked side by side, but are placed in perforated-quartz cages. The cages are positioned beneath long, 10 perforated, quartz reaction-gas injector tubes, one tube for each reactant gas. Gas flows vertically from the injector tubes, through the cage perforations, past the wafers, parallel to the wafer surface and into exhaust slots below the cage. The size, number, and location of cage perforations are used 15 to control the flow of reactant gases to the wafer surfaces. By properly optimizing cage perforation design, each wafer may be supplied with identical quantities of fresh reactants from the vertically adjacent injector tubes. Thus, this design 20 may avoid the wafer-to-wafer reactant depletion effects of the end-feed tube reactors, requires no temperature ramping, produces highly uniform depositions, and reportedly achieves low particulate contamination.

The third major CVD deposition method is PECVD. This method is categorized not only by pressure regime, but also 25 by its method of energy input. Rather than relying solely on thermal energy to initiate and sustain chemical reactions, PECVD uses an rf-induced glow discharge to transfer energy into the reactant gases, allowing the substrate to remain at a lower temperature than in APCVD or LPCVD processes. Lower substrate temperature is the major advantages of PECVD, providing film deposition on substrates not having sufficient thermal stability to accept coating by other methods. PECVD may also enhance deposition rates over those achieved using thermal reactions. Moreover, PECVD 30 may produce films having unique compositions and properties. Desirable properties such as good adhesion, low pinhole density, good step coverage, adequate electrical properties, and compatibility with fine-line pattern transfer processes, have led to application of these films in VLSI.

40 PECVD requires control and optimization of several deposition parameters, including rf power density, frequency, and duty cycle. The deposition process is dependent in a complex and interdependent way on these parameters, as well as on the usual parameters of gas 45 composition, flow rates, temperature, and pressure. Furthermore, as with LPCVD, the PECVD method is surface reaction limited, and adequate substrate temperature control is thus necessary to ensure uniform film thickness.

CVD systems usually contain the following components: 50 gas sources, gas feed lines, mass-flow controllers for metering the gases into the system, a reaction chamber or reactor, a method for heating the wafers onto which the film is to be deposited, and in some types of systems, for adding additional energy by other means, and temperature sensors. 55 LPCVD and PECVD systems also contain pumps for establishing the reduced pressure and exhausting the gases from the chamber.

Suitable solvents for use in such solutions of the present 60 compositions of the present invention include any suitable pure or mixture of organic, organometallic, or inorganic molecules that are volatilized at a desired temperature. Suitable solvents include aprotic solvents, for example, cyclic ketones such as cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone; cyclic amides such as N-alkylpyrrolidinone wherein the alkyl has from about 1 to 65 4 carbon atoms; and N-cyclohexylpyrrolidinone and mixtures thereof. A wide variety of other organic solvents may

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The present composition has a dielectric constant of preferably less than 3.2 and more preferably from about 2.5 to less than 3.2.

The present composition may be used in a desirable all spin-on stacked film as taught by Michael E. Thomas, "Spin-On Stacked Films for Low k_{eff} Dielectrics", *Solid State Technology* (July 2001), incorporated herein in its entirety by reference.

Analytical Test Methods:

Dielectric Constant: The dielectric constant was determined by coating a thin film of aluminum on the cured layer and then doing a capacitance-voltage measurement at 1 MHz and calculating the k value based on the layer thickness.

Shrinkage/Expansion: Film shrinkage or expansion was measured by determining the film thickness before and after the process. Shrinkage was expressed in percent of the original film thickness. Shrinkage was positive if the film thickness decreased. The actual thickness measurements were performed optically using a J. A. Woollam M-88 spectroscopic ellipsometer. A Cauchy model was used to calculate the best fit for Psi and Delta (details on Ellipsometry can be found in e.g. "Spectroscopic Ellipsometry and Reflectometry" by H. G. Thompkins and William A. McGahan, John Wiley and Sons, Inc., 1999).

Refractive Index: The refractive index measurements were performed together with the thickness measurements using a J. A. Woollam M-88 spectroscopic ellipsometer. A Cauchy model was used to calculate the best fit for Psi and Delta. Unless noted otherwise, the refractive index was reported at a wavelength of 633 nm (details on Ellipsometry can be found in e.g. "Spectroscopic Ellipsometry and Reflectometry" by H. G. Thompkins and William A. McGahan, John Wiley and Sons, Inc., 1999).

FTIR analysis: FTIR spectra were taken using a Nicolet Magna 550 FTIR spectrometer in transmission mode. Substrate background spectra were taken on uncoated substrates. Film spectra were taken using the substrate as background. Film spectra were then analyzed for change in peak location and intensity. The results are reported in an absorbance mode.

Isothermal Gravimetric Analysis (ITGA) Weight Loss: Total weight loss was determined on the TA Instruments 2950 Thermogravimetric Analyzer (TGA) used in conjunction with a TA Instruments thermal analysis controller and associated software. A Platinel II Thermocouple and a Standard Furnace with a temperature range of 25° C. to 1000° C. and heating rate of 0.1° C. to 100° C./min were used. A small amount of sample (7 to 12 mg) was weighed on the TGA's balance (resolution: 0.1 µg; accuracy: to ±0.1%) and heated on a platinum pan. Samples were heated under nitrogen with a purge rate of 100 ml/min (60 ml/min going to the furnace and 40 ml/min to the balance).

Tape Test: The tape test was performed following the guidelines given in ASTM D3359-95. A grid was scribed into the dielectric layer according to the following. A tape test was performed across the grid marking in the following manner: (1) a piece of adhesive tape, preferably Scotch brand #3 m600-1/2X1296, was placed on the present layer, and pressed down firmly to make good contact; and (2) the tape was then pulled off rapidly and evenly at an angle of 180° to the layer surface. The sample was considered to pass if the layer remained intact on the wafer, or to have failed if part or all of the film pulled up with the tape.

Particle Count: Film particles counts were measured on a KLA 6420 Surfscan. An oxide recipe with a film thickness matching the product film thickness was used. The recipe was set up with the lowest size threshold to be 0.2 microns. The particle number reported is the total number of particles detected above the size threshold.

Candela Film: Wafers were analyzed with a Candela OSA and spun at 5000 rpm for the measurements. The data was

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acquired using S-specular acquisition mode with 50 microns track spacing and 16K data points per track. The resulting images were inspected visually for defects. No quantitative analysis was performed.

Contact Angle: The contact angle measurement was performed to determine the contact angle of the dielectric solution on the inventive product in order to create a Si-wafer/dielectric/inventive product/dielectric stack. A VCA2500 Video Contact Angle System from ASC Products was used to perform the measurements. In preparation for the measurement, the wafer was coated with the first dielectric layer and then the inventive product layer. For the measurement, a droplet of the dielectric solution which was to be deposited as the top layer was brought in contact with the inventive product surface. The droplet volume was set to 0.8 microliter. The video image was captured for the next 3.5 seconds beginning with time when the droplet was formed on the surface. The contact angle was then measured on the captured video image using the contact angle measurement software. The average of five measurements is reported.

EXAMPLES

Comparative A:

Organosilsesquioxanes having 60–80% alkyl groups having 4 carbons or less and 20–40% hydrogen dewetted or had poor wetting with the organic dielectric of commonly assigned pending patent application U.S. Serial No. 60/350, 187 filed Jan. 15, 2002. Such organosiloxanes had the required minimum of at least 50% methyl groups taught by U.S. Pat. No. 4,626,556; the contact angle with the aforementioned organic dielectric ranged from 15–39°. Such organosiloxanes also included Honeywell HOSP® product comprising about 80% methyl groups and 20% hydrogen groups; the contact angle of HOSP® product with the aforementioned organic dielectric was 35°.

Comparative B:

FIG. 1 shows the TGA results for Honeywell Accuglass® 720 product comprising organosiloxane with 66% phenyl and 34% methyl. The program was: (a) ramp to 200° C. and hold for 15 minutes at 200° C., (b) then ramp to 430° C. and hold for 90 minutes at 430° C., and (c) two cycles ramping from 200° C. to 450° C. with a hold at 450° C. for 30 minutes. Based on the TGA, the weight loss was 1.9 percent per hour.

AlliedSignal Inc.'s HOSP™ Product Bulletins (dated November 1998 and February 1999) teach that HOSP™ polymer is thermally stable to 550° C. and Honeywell's "Integration of HOSP® in Cu-Damascene Interconnect", IITC 2000 teaches that HOSP® polymer has TDMS stability to >450° C. However, when we subjected HOSP® polymer comprising organosiloxane having 80% methyl groups and 20% hydrogen to the current more stringent TGA test, the weight loss was 0.56 percent per hour as shown in FIG. 2.

We also made an organosiloxane comprising 50% phenyl groups and 50% hydrogen as covered by commonly assigned U.S. Pat. Nos. 5,973,095; 6,020,410; 6,043,330; 6,177,143; and 6,287,477. FIG. 3 shows the TGA results for this product. Based on the TGA, the weight loss was 1.0 percent per hour.

Examples 1–14

For Examples 1 and 3, a reactor was warmed up to 35° C. The following were added to the reactor: toluene (900 milliliters), 10% t-BACl in water (24.0 grams), deionized water (23.4 grams), and ethanol (8.0 grams) with stirring. Separately, a silane mixture was prepared in a teflon bottle by adding: phenyl trichlorosilane (81.0 grams), vinyl trichlorosilane (61.8 grams), and trichlorosilane (69.1 grams). Toluene (100 milliliters) was added to the mixture. Using a peristaltic pump, the silane mixture was added into reactor